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Geology and Mineralogy of the Apex Germanium-Gallium Mine, Washington County, Utah

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Geology and Mineralogy of the Apex Germanium-Gallium Mine, Washington County, Utah

By LAWRENCE R. BERNSTEIN

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Geology and Mineralogy of the Apex Germanium-Gallium Mine, Washington County, Utah

By Lawrence R. Bernstein

Abstract

The Apex Mine, in Washington County, southwestern Utah, is the first mine in the world to be operated primarily for germanium and gallium. The ore, consisting of goethite, limonite, hematite, jarosite, azurite, malachite, conichalcite, and several other metal oxides, carbonates, arsenates, and sulfates, is thoroughly oxidized to at least 425 m below the surface. Most of the copper-rich ore was removed during previous mining operations, leaving behind the iron-rich minerals that contain most of the germanium and gallium. Germanium is concentrated chiefly in goethite (as much as 0.5 percent), hematite (as much as 0.7 percent), and limonite (as much as 0.5 percent), while gallium is concentrated mostly in jarosite (as much as 0.7 percent) and in some limonite (as much as 2 percent). Copper minerals are concentrated in and adjacent to carbonate rock, apparently replacing it. The ore at the Apex Mine forms an irregular, branching, chimney-like body (or bodies) in fault breccia, gouge, and fissures associated with steeply dipping subparallel fault zones in the Pennsylvanian Callville Limestone. Within and immediately adjacent to the fault zones, limestone has been dolomitized and locally silicified. Only a few small pieces of unreplaced primary sulfide ore have been found; these contain pyrite, galena, sphalerite, chalcopyrite, quartz, and traces of barite. The abundance of copper, germanium, gallium, and arsenic in the supergene ore implies the former presence of sulfides and sulfosalts containing these metals in the primary ore, which would make it similar to dolomite-hosted ores at Kipushi, Zaire; Tsumeb, Namibia; and Ruby Creek, Alaska. High concentrations of germanium and gallium should be looked for in gossans and other oxidized zones of copper-rich, arsenic-bearing sulfide deposits, particularly those in carbonate host rocks.

INTRODUCTION

Germanium and Gallium

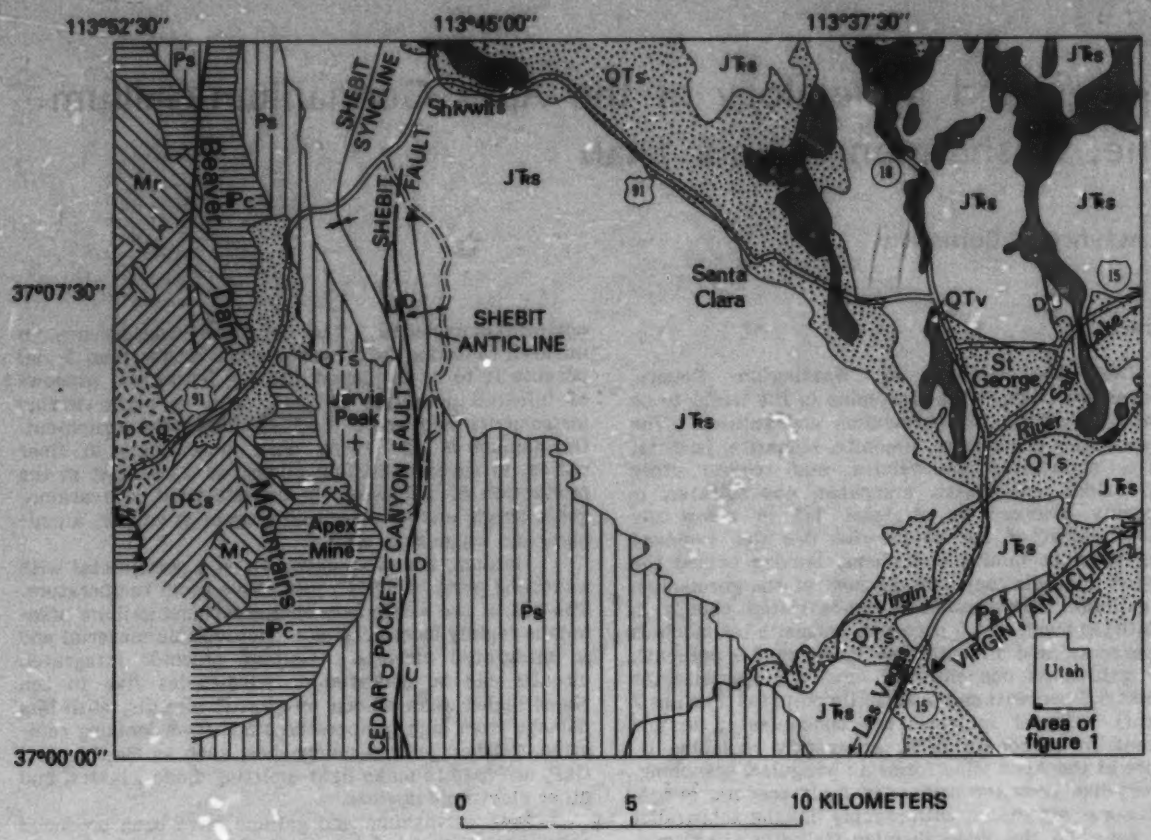
The rare elements germanium and gallium are of increasing use in a variety of high-technology products. Germanium, atomic number 32, is a semiconducting metalloid that has a gray color, metallic luster, and conchoidal fracture. It was used to make the first transistor in 1948, and it continues to be an industrially important electronic material. The primary electronic applications of germanium at present are in X-ray and gamma-ray detectors and in high-frequency integrated circuits. Germanium is most used, however, in infrared optical components. The element's transparency to infrared radiation (with wavelengths longer than 2 μm) permits it to be fashioned into the lenses and windows of infrared detection devices, such as night-viewing instruments and some medical diagnostic equipment. Germanium is also being used increasingly in fiber optics, in superconducting alloys, as a catalyst in the production of polyester, in experimental anticarcinogenic drugs, and as a hardening agent in copper, aluminum, and magnesium alloys.

Gallium, atomic number 31, is a semi-metal with a melting point of 30 °C, just above room temperature. The use of the semiconducting compound gallium arsenide is rapidly increasing as a photovoltaic material and in integrated circuits. Gallium arsenide integrated circuits can be operated at frequencies five to ten times higher than silicon integrated circuits, with less damage from high temperatures and from ionizing radiation. Other gallium compounds, such as GaAlAs and GaP, are used to make light-emitting diodes, lasers, and other electronic devices.

Both germanium and gallium have been produced only as byproducts of ore processing—germanium mostly from sphalerite-rich ores, and gallium mostly from bauxite. Because of increasing demand for these two elements, new sources are being sought. The Apex Mine is the first in the world to be operated primarily for germanium and gallium, and is the first to mine oxidized sulfide ore for these elements.

Apex Mine

The Apex Mine (also called the Dixie Mine) is located on the east flank of the Beaver Dam Mountains in Washington County, Utah, about 22.5 km west of St. George and 9 km north of the Arizona border (fig. 1). The main adit is at an elevation of 1,656 m, lat 37°4'11" N. and long 113°48'14" W. (NE¼SW¼SW¼ sec. 6, T. 43 S., R. 17 W.). Before it was reopened in 1985 for germanium and gallium, the mine was operated intermittently from 1884 to 1962, producing over 7,000 mt of copper, 400 mt of lead, 180,000 troy oz of silver, and minor zinc and gold (Perry and McCarthy, 1977, p. 516-525). The ore at the Apex Mine consists of goethite, limonite, hematite, azurite, malachite, conichalcite, jarosite, and minor amounts of other metal carbonates, oxides, sulfates, and arsenates. These minerals occur in dolomitized and silicified breccia, gouge, and fissures in steeply dipping fault zones within the gently dipping Pennsylvanian Callville Limestone. Germanium is concentrated mostly in the goethite, hematite, and limonite, whereas gallium is concentrated chiefly in jarosite and in some limonite. These iron-rich minerals were



EXPLANATION

- QTs — Surficial deposits and sedimentary rocks (Quaternary and Tertiary)
- QTv — Volcanic rocks (Quaternary and Tertiary) —Basaltic lava flows
- JTrs — Sedimentary rocks (Jurassic and Triassic)
- Ps — Sedimentary rocks (Permian)
- Pc — Callville Limestone (Pennsylvanian)
- Mr — Redwall Limestone (Mississippian)
- DCs — Sedimentary rocks (Devonian to Cambrian)
- pCg — Gneiss, schist, and granitic rocks (Precambrian)
- Contact—Dashed where inferred
- Fault—Dashed where inferred. U, upthrown side; D, downthrown side
- Thrust fault—Sawteeth on upper plate
- Anticline—Showing direction of plunge
- Syncline

Figure 1. Location of Apex Mine, Washington County, Utah, and generalized geology of surrounding region. Geology modified from Cook (1960).

generally rejected as waste during the previous mining operations. Copper, iron, lead, zinc, and silver are recovered as byproducts from the current mining operations.

This report provides an outline of the geology and mineralogy at the Apex Mine as known to October 1985. Possible analogies to other deposits, and a proposed model for the genesis of the ore, are also described.

ACKNOWLEDGMENTS

I am very grateful to Bernard Dewonck of Musto Explorations Limited for guiding me through the Apex Mine, permitting me to take samples, allowing me to use some assay data acquired by Musto, and discussing the deposit. I also thank J.E. Dutrizac of CANMET in Ottawa, Canada, for sending a preprint of his paper on gallium and germanium host minerals at the Apex Mine. Funding for this project was provided in part by a Shell Foundation grant through Stanford University.

METHODS

The Apex Mine was visited by the author for four days in mid-April 1985. Underground workings, including a decline ramp and four crosscuts down to the 1,601-m level, were examined and sampled. The collapsed shaft and adit of the much smaller Paymaster Mine, 275 m south-southeast of the Apex Mine on the same fault zone, were examined at the surface. Other outcrops of the ore zone and host rocks were also observed and sampled, as were the extensive tailings from the old mine workings. Several additional samples were obtained from diamond-drill cores at the Apex Mine. The samples were analyzed using an automated Rigaku powder X-ray diffractometer at Stanford University, and a Cambridge Stereoscan scanning electron microscope (SEM) with an energy-dispersive X-ray elemental analyzer at the U.S. Geological Survey, Menlo Park, California.

Assays of several ore samples were performed by Acme Analytical Laboratories of Vancouver, Canada, who used inductively coupled argon plasma analysis (ICP) to measure the concentrations of Cu, Pb, Zn, Ag, Co, Ni, Mo, Bi, As, Sb, Cd, W, Au, and Si in samples fused with lithium metaborate. Germanium and gallium were measured, with a detection limit of 1 ppm, by graphite furnace atomic absorption spectroscopy on samples dissolved in hot aqua-regia and hydrofluoric acid in a pressure bomb. Carbon dioxide was measured by infrared spectroscopy of gas released during heating in a furnace; carbon not present as carbonate was determined by taking the difference in measurements between untreated samples and samples that had been leached in acid to release all the CO_2.

Semiquantitative emission spectrographic analyses were performed on seven additional samples by Richard Lerner of the U.S. Geological Survey. These analyses were made on hand-picked samples, about 500 mg each, of homogeneous-appearing ore material. Elements Ge and In were analyzed by a 6-step visual semiquantitative procedure using glass plates, whereas the other elements were analyzed using a direct-reading emission spectrophotometer. Owing to their high iron content, the samples were diluted with material containing Si, Al, and K to minimize interferences; this raised detection limits, and also made measurements for Si, Al, and K less accurate (standard deviations of 30-50 percent of the recorded value, versus 10-20 percent for the other elements).

GEOLOGIC SETTING

Regional Geology

The Apex Mine is on the east slope of the Beaver Dam Mountains, a northwest-trending uplift at the boundary between the Basin and Range province to the west and the Colorado Plateau to the east. The Pennsylvanian Callville Limestone, which hosts the ore, crops out on the eastern and southern slopes of the mountains, where it rests on Mississippian Redwall Limestone and is overlain by Permian Pakoon Limestone (Cook, 1960; Steed, 1980). In the Beaver Dam Mountains and Virgin River Gorge (about 11 km south-southwest of the Apex Mine) the shallow-marine Callville is 200-210 m thick (Steed, 1980). Igneous rocks are not known in the vicinity of the Apex Mine, though fresh-looking Quaternary basaltic lava flows occur 13 km to the north-northeast near Shivwits.

Local Geology

In the vicinity of the mine, the Callville Limestone consists of gently dipping beds typically a few centimeters thick (fig. 2), though locally they are as much as 6 m thick. The bedding generally dips 5° to 10° E. to N., with local warps producing dips up to 5°

Figure 2. Main adit to Apex Mine, Washington County, Utah, showing gently dipping beds of the Callville Limestone.

W., and is commonly irregular and discontinuous. Irregular chert nodules as much as 50 cm across, which locally form short discontinuous layers, are abundant; quartz in these nodules is commonly recrystallized to grains as much as several millimeters across. Rounded quartz grains as much as a few millimeters across are locally common in the limestone, and discontinuous sandstone beds as much as several meters thick occur in places. Scattered shaly beds, as much as a few centimeters thick, are also present, as are some dolomitic zones. Poorly preserved fossil horn corals are locally common. Solution cavities that range from vugs a few centimeters across to caves several meters across are found in the mine; these generally contain small stalactites or euhedral calcite crystals.

The most prominent structural feature near the mine is the Apex fault, which strikes north-northwest and dips 64° to 71° W. (fig. 3). The fault is readily observed at the shafts of the Apex and Paymaster mines where the sheared and brecciated zone is 5-7 m wide, but elsewhere it is covered by slopewash and is apparently narrower. The fault can be approximately traced at the surface by the sporadic presence of iron oxides, azurite, and malachite in the slopewash. At the Apex and Paymaster shafts, the fault zone consists of limonite- and goethite-impregnated gouge that contains small amounts of malachite and azurite, with dolomite breccia in the footwall and apparently unaffected limestone in the hanging wall. The dolomite breccia observed at the surface has angular to subrounded dolomite clasts in a fine-grained dolomite matrix, whereas that in the mine commonly has a limonite-goethite matrix. Evidence on the direction of displacement for the fault was not observed. Kinkel (1951) mapped a distinctive sandstone bed and proposed the fault to be reverse with a vertical displacement of about 75 m.

Ore Geology

The ore at the Apex Mine is defined as a goethite-limonite-hematite zone that contains local concentrations of jarosite, azurite, malachite, and other supergene copper, iron, lead, and zinc minerals. This zone forms a highly irregular, branching, chimney-like body (or bodies) within breccia, gouge, and fissures associated with numerous subparallel faults in the footwall of the Apex fault. Mining and drilling data are currently insufficient to define the irregular shape of the ore zone or zones, but ore thicknesses of 1 to about 20 m can be observed, with a northwest strike length of at least 107 m confirmed by drilling (Lalonde, 1983).

The texture of the ore zone varies considerably. Most of the ore consists of broken fragments and stringers of goethite or hematite in a matrix of limonite (here used to denote soft iron oxides and hydroxides that give a weak to non-existent powder X-ray diffraction pattern). In places only limonite is present, whereas in other places (generally at the footwall of the ore zone) hard, vuggy goethite is present. Vugs in this goethite range in size from a few millimeters to several centimeters across, and commonly contain botryoidal crusts or euhedral crystals of azurite, malachite, conichalcite, rosasite, or brochantite. In appearance, such ore resembles the gossans of many sulfide deposits, particularly those that contain arsenates such as that at Mapimi, Mexico (Hoffmann, 1968). Limonite-matrix dolomite breccia occurs in places, and the

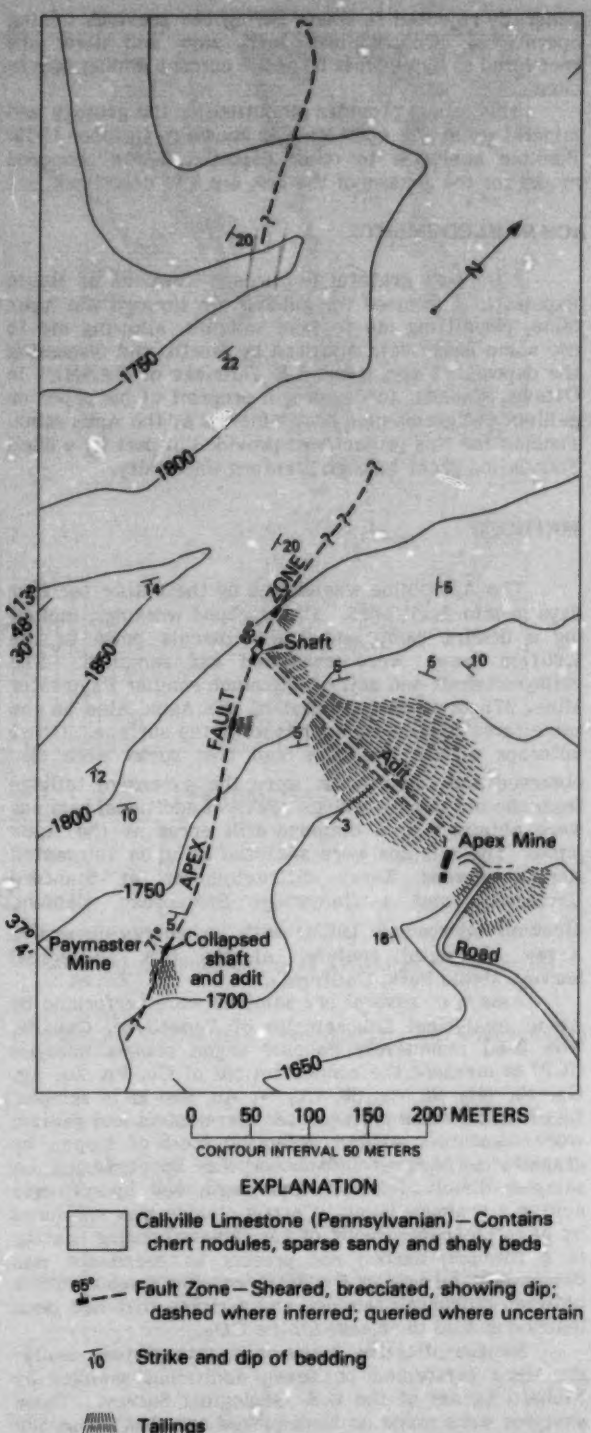


Figure 3. Locations of Apex and Paymaster mines and Apex fault zone, Washington County, Utah. Compiled from Kinkel (1951) and field work by L. R. Bernstein, April, 1985. Most of the tailings shown on this map were hauled to the mill site, about 9 km to the north-northeast, during the summer of 1985.

dolomite clasts commonly have a rim of malachite or azurite. Jarosite occurs as discrete mustard-yellow to brownish-yellow, sparkly zones as much as 1.5 m thick. It also occurs in the matrix of some dolomite breccia, and is disseminated in small amounts throughout much of the ore. The copper minerals appear to be concentrated toward the hanging wall of the ore zone adjacent to dolomite. They also replace dolomite fragments within limonite-goethite ore, and are disseminated through much of the ore in small quantities. Contacts between the ore and wall rocks are commonly gradational, with fracture coatings of limonite extending several meters into the wall rocks.

Limestone within the ore zone has been converted to dolomite or microcrystalline quartz, and the effects of dolomitization and silicification locally extend 1-2 m into the wall rocks. Dolomitization was pervasive throughout the ore and fault zones, whereas silicification appears to have been most intense toward the hanging wall and at depth.

As the extent of the ore zone has not yet been fully defined, particularly at depth, grade and tonnage estimates are preliminary. The ore defined as of October 1983 is estimated by Lalonde (1983) to be 242,768 short tons containing 0.064 percent Ge, 0.032 percent Ga, 1.63 percent Cu, 0.77 percent Pb, 1.58 percent Zn, 0.50 percent As, 16.73 percent Fe, and 1.21 troy oz/short ton (38 ppm) Ag. In addition, the surface dump from the old mine is estimated (Lalonde, 1983) to contain about 50,000 short tons with 0.037 percent Ge, 0.019 percent Ga, and 1.55 percent Cu. Chemical analyses of some representative ore samples are presented in table 1; chemical analyses of some homogeneous-appearing, nearly monomineralic samples are presented in table 2.

Table 1. Chemical analyses of some representative ore samples from Apex Mine, Washington County, Utah

[Compositions determined by inductively coupled argon plasma analysis for Cu, Pb, Zn, As, Bi, Cd, Co, Mo, Ni, Sb, Fe, Ag, Ca, Mg, and Si; atomic absorption for Ge and Ga; and infrared spectroscopy for CO_2. Analyses performed by Acme Analytical Laboratories, Vancouver, Canada; provided through the courtesy of Musto Explorations Ltd.]

Sample[1] No.—	1	2	3	4	5	6	7	8
	Weight percent							
Ge	0.026	0.198	0.460	0.382	0.108	0.224	0.065	0.092
Ga	.032	.033	.086	.148	.119	.086	.040	.087
Cu	3.08	.65	.16	12.00	.10	.31	.17	1.42
Pb	.09	.51	.10	.42	.74	5.48	4.10	.87
Zn	1.59	1.06	.33	.62	.13	.26	.12	.53
As	.09	1.10	2.10	4.38	.70	2.74	1.03	2.71
Bi	0.001	0.01	0.01	0.001	0.01	0.001	0.004	0.053
Cd	.00	.01	.01	.01	.00	.001	.001	.00
Co	.01	.01	.01	.04	.00	.001	.001	.01
Mo	.004	.032	.027	.038	.039	.013	.043	.057
Ni	.03	.02	.02	.06	.01	.01	.01	.01
Sb	.001	.012	.089	.077	.055	.037	.143	.257
Fe	26.18	40.70	31.92	19.20	12.12	25.43	22.36	14.05
Ca	1.73	.16	.42	1.31	.11	.35	.14	.58
Mg	1.23	.06	.09	.07	.06	.04	.02	.05
SiO_2	41.58	25.24	37.04	41.23	69.48	30.12	28.95	65.74
CO_2	5.54	.49	.33	4.36	.37	.24	.14	.61
	Parts per million							
Ag	3	8	77	161	97	197	235	674

[1]Sample descriptions (some quartz is present in all the samples): 1. Dense, vuggy goethite with some limonite. 1,630-m (5,347-ft) level, N. rib. 2. Mainly dense, vuggy goethite. DDH85-9, near 29 m (96 ft). 3. Mixed, fractured goethite, hematite, limonite. DDH85-9, 45-47 m (148.5-155 ft). 4. Friable goethite with azurite, conichalcite, and some plumbian jarosite. 1,625-m (5,330-ft) level, S. rib. 5. Mixed friable goethite, limonite, and a little plumbian jarosite. DDH85-9, 44-45 m (143.5-148.5 ft). 6. Laminated, earthy, red-brown limonite and yellow plumbian jarosite. 1,601-m (5,253-ft) level, N. rib. 7. Mostly plumbian jarosite. 1,601-m (5,253-ft) level, N. rib. 8. Mostly slightly plumbian jarosite. 1,625-m (5,330-ft) level, S. rib.

MINERALOGY

Primary Ore

The ore has been thoroughly oxidized to at least 425 m below the surface (the maximum depth of the old workings), and only a few fragments of sulfide minerals have been found. Several pieces of coarsely crystallized galena, as much as 10 cm across, have been found on the old dump, embedded in and largely replaced by anglesite. Within the galena and adjacent anglesite are masses of fine-grained pyrite, as much as 1 cm across, sooty black covellite that replaces pre-existing Cu-bearing sulfides, and very scarce grains of residual chalcopyrite up to 100 μm across. Lalonde (1983) reported very fine grained galena disseminated in a mustard yellow mud (plumbian jarosite) in drill-hole 83-16 at 48.8 m (160 ft). He also reported dark-gray to black quartz-pyrite-sphalerite stringers in limonitic zones in drill-holes 83-20 and 83-25. In drill-hole 85-1 at 28.3 m (93 ft) a layer of fine-grained pyrite, 4 cm thick, was found in the center of a mass of dense goethite. Small amounts of barite and quartz are intergrown with the pyrite. In the SEM, scarce scattered grains of galena 1-10 μm across were observed, as were a few grains of an unidentified Pb- As- Cu- S-rich mineral, 1-5 μm across. Approximately 75 ppm Ni and 15 ppm Co were detected in this pyrite (table 2). In drill-hole 85-36 at 67.1 m (220 ft) friable masses of marcasite several centimeters across occur, together with veinlets and blebs of covellite as much as one millimeter wide. The marcasite occurs in two habits: intergrown euhedral tabular to lozenge-shaped crystals, 0.1-0.7 mm long, and spongy, anhedral material filling interstices between the euhedral crystals. It is not clear whether the marcasite is of hypogene or supergene origin.

Supergene Ore

Goethite—Goethite is the most abundant mineral in the ore zone, and occurs in several habits. It is most common as irregular fragments of stringers as much as several centimeters across mixed with fine-grained quartz, imbedded in limonite or jarosite that form yellow-brown locally friable masses. It also occurs as zones of hard, dense, brown, vuggy material, particularly toward the footwall. In the SEM, this material is found to be intimately admixed with microcrystalline quartz, accounting for its hardness. A few masses of dense lustrous goethite a few centimeters across having a conchoidal fracture were found.

Goethite is the major host for germanium, and contains as much as 5300 ppm Ge (Dutrizac and others, in press). In the SEM, no discrete germanium minerals were observed, and the germanium appears to be distributed rather uniformly in the goethite itself (either within the crystal lattice or in grain boundaries). Typical, clean-looking areas of goethite were always found to contain as much as several percent of Si, Al, Ca, K, As, and Zn, with traces of Pb and Ge. The hard

Table 2. Chemical analyses of some nearly monomineralic samples from Apex Mine, Washington County, Utah

[Compositions determined by semiquantitative emission spectroscopy performed by K. Lorner of the U.S. Geological Survey. Standard deviations are about 10-20 percent of the indicated value, except for Si, K, and Al, for which they are 30-50 percent. Elements not detected at the indicated detection limits (ppm) for samples 2-7 (detection limits for sample 1 are 40% of these, due to less sample dilution): Au(50),Be(5),Co(500),Cr(50),Hg(2500), In(7),La(100),Li(250),Mn(1000),Nb(125),P(1000),Re(250),Sc(50),Sn(1000), Sr(50),Te(250),W(500),Y(50),Zr(100).]

Sample[1] No.—	1	2	3	4	5	6	7
Parts per million							
Ge	<7	150	7000	3000	2000	2000	3000
Ga	<20	<50	150	100	100	200	150
Cu	1900	250	620	1500	>5000	1800	1300
Pb	>5000	290	110	>5000	1600	330	5000
Zn	<100	1100	1500	>5000	>5000	2600	1000
As	<400	<1000	>5000	>5000	>5000	>5000	>5000
Ag	66	<5	45	100	<5	48	1200
B	<20	<50	50	<50	<50	50	<50
Ba	<40	640	150	410	<100	150	420
Bi	<20	<50	<50	<50	<50	<50	80
Cd	<8	<20	50	50	50	100	<20
Ca	<2	15	37	70	100	100	70
Mo	<20	<50	30	<50	<50	50	950
Ni	18	75	130	80	250	200	43
Sb	<200	<500	1200	<500	<500	<500	4200
Sr	610	650	2900	750	920	4300	>5000
Ti	<20	<30	<30	<30	<30	<30	170
V	<20	<50	<50	<50	55	<50	<50
Weight percent							
Fe	0.36	50.	34.	45.	46.	29.	20.
Ti	<.04	<.10	.15	<.10	<.10	.15	<.10
Al	<.25	.40	2.0	0.46	.83	2.3	.85
Ca	<.10	<.25	.40	1.2	.25	.80	<.25
Mg	<.20	.70	.65	.70	.70	.60	<.50
K	<.08	.15	1.5	.30	.20	.10	2.0
Na	<.30	<.75	<.75	<.75	<.75	<.75	1.0
SiO_2	<16.	<16.	31.	<16.	22.	36.	25.

[1]Samples: 1. Galena with a few percent anglesite. Tailings of old workings. 2. Pyrite with a few percent of quartz plus traces of barite and galena. DDH85-1, 27 m (93 ft). 3. Granular hematite with intimately intergrown microcrystalline quartz plus small amounts of jarosite and possibly other minerals. DDH85-9, 45-47 m (148.5-155 ft). 4. Reddish-brown limonite with a few percent of jarosite. 1,601-m (5,253-ft) level, N. rib. 5. Dense, vuggy goethite with microcrystalline quartz plus small amounts of jarosite and possibly other minerals. DDH85-9, 29 m (96 ft). 6. Goethite with microcrystalline quartz plus small amounts of jarosite and possibly other minerals. DDH85-9, 45-47 m (148.5-155 ft). 7. Slightly plumbian jarosite with microcrystalline quartz. 1,625-m (5330-ft) level, E. rib.

conchoidal material contains the smallest amounts of all these elements. Discrete hexagonal plates of jarosite 5-10 μm across are dispersed in much of the goethite.

Limonite—The term limonite is used to denote the abundant yellow-brown to red-brown, friable, commonly earthy mixture of iron-rich oxides, hydroxides, and oxysalts that produce only small, broad peaks (if any) in powder X-ray diffraction patterns. Quartz and goethite are almost always present, but most of this material is either amorphous or is so fine grained that it will not produce sharp diffraction peaks. Limonite occurs (1) interstitially to goethite and hematite, (2) as the matrix of some dolomite breccia, (3) impregnating fault gouge, and (4) as vug and fracture fillings throughout the ore. An area of laminated red-brown, earthy limonite was observed in the north rib of the 1601-m crosscut that contains numerous parallel layers, about 1-2 mm thick, of yellow plumbian jarosite, suggestive of a banded texture in the primary sulfide ore (see analysis 6, table 1). In the SEM, limonite samples are found to contain as much as several percent Si, Ca, Al, K, As, Pb, Cu, and Zn. Gallium is not usually detected in the SEM (< 500 ppm), but zones of limonite a few tens of micrometers across that contain as much as 2 weight percent Ga were observed in the laminated sample (analysis 6, table 1). These small zones also contain 1-2 weight percent Ca, Pb, As, K, and Al. Germanium is detected using the SEM in many limonite samples (500 ppm to about 2,000 ppm), but not in others.

Hematite—Hematite is much less abundant than goethite or limonite and occurs as red-brown, hard nodules and angular fragments encrusted with limonite and jarosite. It is admixed with abundant fine-grained (< 1 μm) quartz. The hematite contains as much as several percent Si, Ca, K, and As, and somewhat more Ge than was observed in goethite. Emission spectroscopy detected roughly 7,000 ppm Ge in one specimen (table 2). The extreme fine-grained (< 1 μm) nature of this material makes the host(s) for these elements uncertain. Powder X-ray diffraction detected only hematite and quartz. Adsorption of some of the minor elements in grain boundaries is a possibility.

Jarosite—Massive jarosite is bright yellow to brownish yellow, slippery feeling, and has a fine-grained sparkly appearance. It forms zones at least 1.5 m thick, and also occurs in breccia matrix and dispersed in smaller quantities throughout much of the ore. Under the SEM it is seen to consist of platy hexagonal crystals, 5-10 μm across, that are always mixed with quartz, which is fibrous in some specimens (fig. 4). It contains variable amounts of Pb, Na and K, being intermediate between jarosite, natrojarosite, and plumbojarosite. Dutrizac and others (in press) and the current study found the cell parameters, as determined by powder X-ray diffraction techniques, to lie between those of the two end members, without the doubling of the c-axis found for plumbojarosite. Jarosite is a major host for Ga in the ore, with as much as 0.70 weight percent Ga substituting for Fe according to Dutrizac and others (in press). They reported an average composition, based on 11 electron microprobe analyses, to be: $(K_{0.682}Na_{0.166}Pb_{0.183}Ag_{0.034})_{1.02}(Fe_{2.953}Zn_{0.016}Ga_{0.027})_{3.00}(SO_4)_{2.00}(OH)_{5.96}$. Jarosite is a major host for Ag, which substitutes for K, Na, and Pb (see tables 1 and 2). The cores of many jarosite crystals are occupied by rhombohedral crystals of goyazite-svanbergite 1-10 μm across.

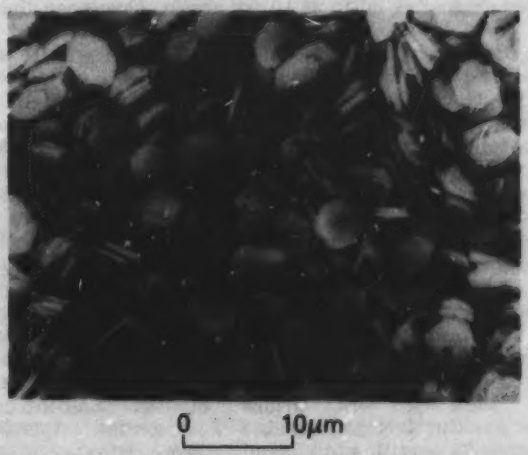


Figure 4. Scanning electron photomicrograph showing tabular, hexagonal jarosite crystals with some acicular quartz crystals. Apex Mine, Washington County, Utah, 1,601-m level.

Goyazite-svanbergite—Dutrizac and others (in press) report the presence of rhombohedral crystals, about 10 μm on edge, of sulfate-bearing goyazite, $SrAl_3(PO_4)_2(OH)_5 \cdot H_2O$, forming a solid solution with svanbergite, $SrAl_3(PO_4)(SO_4)(OH)_6$, in two samples of jarosite. Measureable quantities of Ge and Ga were not detected (< 300 ppm). Similar crystals were observed in this study together with jarosite from the 1,625-m level. Most of these goyazite-svanbergite crystals form the cores of jarosite crystals. Small amounts of As (1,000-7,000 ppm) were detected in this mineral under the SEM.

Azurite—From observations of the underground workings and of the old dump, azurite, $Cu_3(CO_3)_2(OH)_2$, appears to be the most abundant copper mineral in the ore. However, because most of the high-grade copper ore was previously mined out, the content of azurite in the original ore may have been different. Azurite is most concentrated where it fills cavities that are at least several centimeters wide in partly silicified dolomite in the hanging wall. In these cavities it forms botryoidal crusts, as much as 2 cm thick, covered by drusy crystals, as much as a few millimeters across. Azurite also occurs as euhedral crystals, as much as a few millimeters across, lining vugs in goethite, and as partial replacements of isolated dolomite fragments in the limonite-goethite ore. In some places azurite is replaced by malachite, and in other places it is replaced by X-ray-amorphous light-blue chrysocolla-like material.

Malachite—Malachite, $Cu_2CO_3(OH)_2$, is less abundant than azurite, though both minerals occur in the same environments. It forms botryoidal crusts of radial-fibrous crystals as much as 1 cm thick and, locally, it replaces azurite. In places, spheres of radiating fibrous crystals that are several millimeters across are observed on goethite.

Conichalcite—Conichalcite, $CaCu(AsO_4)(OH)$, is nearly as common as malachite. It forms thin emerald-green crusts on goethite, generally associated with azurite.

Aurichalcite—Aurichalcite, $(Zn,Cu)_5(CO_3)_2(OH)_6$, is sparsely found in goethite as turquoise-blue radiating fibrous crystals as much as 1 cm long. It is generally not associated with the other copper minerals.

Rosasite—A few blue-green spheres of radiating fibrous crystals of rosasite, $(Cu,Zn)_2(CO_3)(OH)_2$, that are several millimeters across were found in vuggy goethite with malachite, azurite, and conichalcite.

Brochantite—Brochantite, $Cu_4SO_4(OH)_6$, was found in a sample of hard vuggy goethite on the dump, where it forms transparent, green, euhedral crystals that are a few millimeters across on a crust of malachite.

Cuprite—A lens of cuprite (Cu_2O), about 30x23x8 mm, was observed in drill-hole 85-12 at 22.7 m (74.5 ft). The cuprite has an average grain size of about 0.5 mm. The lens is surrounded by a crust of malachite, which is in turn surrounded by a crust of azurite, which is enclosed within earthy decomposed dolomite containing clay minerals and limonite. Malachite has replaced cuprite within the lens along fractures.

Anglesite—White, gray, and yellow massive anglesite ($PbSO_4$) surrounds and partly replaces galena in a sample from the dump. No elements other than Pb and S were detected in the SEM.

Covellite—Sooty bluish-black covellite (CuS) masses that are as much as 1 cm across occur with pyrite, anglesite, and traces of chalcopyrite in a sample of coarse-grained galena found on the dump. Small amounts of covellite occur in fractures within the galena crystals. Veinlets and blebs of covellite, as much as one millimeter wide, occur with massive marcasite in drill hole 85-36 at 67.1 m (220 ft).

Black manganese oxides—Thin coatings of black manganese oxides occur locally in fractures and vugs in goethite. A high concentration of these black oxides was noted in goethite at the 1,625-m (5,330-ft) level together with azurite and conichalcite.

Chrysocolla—X-ray-amorphous, light-blue, chalky to hard material that have a conchoidal fracture is a common late alteration product of azurite in cavities.

Other reported minerals—Bullock (1967) reported the presence of native copper, cerussite, hydrozincite, adamite, and smithsonite from the Apex Mine, though these were not observed in the present study.

DISCUSSION AND CONCLUSIONS

Primary Ore Deposition

Deposition of ore at the Apex Mine was confined to brecciated, fissured, and sheared zones associated with the Apex fault. As only one geologic formation (Callville Limestone) is present, structural data on the geologic ages of faulting and of ore deposition are not available. Kinkel (1951) noted that although the limestone has abundant solution cavities, only those directly connected with the fault zone were mineralized. Dolomitization and silicification were associated with the fault zone, and extended as much as several meters beyond the ore into the wallrocks.

No large examples of primary ore have been found at the Apex Mine, but aspects of its composition can be inferred. The ore was certainly rich in iron and copper. It also contained considerable lead, lesser zinc and arsenic, and small amounts of germanium and gallium. It is very unlikely that germanium and gallium were introduced during supergene alteration, as these elements are always highly depleted in carbonate rocks (by roughly two orders of magnitude) in relation to their average crustal abundance (Bernstein, 1985; Burton and others, 1959). The available fragments of primary ore show the presence of fine grained pyrite, which was probably abundant, coarse and fine grained galena, sphalerite, chalcopyrite, and a small amount of barite. The abundance of secondary copper minerals now observed indicates the former presence of abundant copper-bearing sulfides such as bornite, chalcopyrite, and chalcocite. The abundance of arsenic in the secondary copper and lead minerals strongly suggests the former presence of sulfosalts such as tennantite or lead-arsenic sulfosalts. Significantly, the relatively high concentrations of germanium and gallium indicate that sulfides containing these elements were present. Such sulfides possibly included renierite ($Cu_{11-x}Zn_xGe_{2-x}As_xFe_4S_{16}$), germanite ($Cu_{11}Ge(Cu,Ge,Fe,Zn,W,Mo,As,V)_{4-8}S_{16}$), and gallite ($CuGaS_2$). The relatively small amount of zinc in the ore precludes the possibility that sphalerite was the major host for germanium and gallium.

The inferred primary ore is similar to bornite-chalcopyrite-tennantite±galena±sphalerite ore found at Tsumeb, Namibia (Söhnge, 1964), Kipushi, Zaire

(Intiomale and Oosterbosch, 1974), and Ruby Creek, Alaska (Bernstein and Cox, in press). Ore at these deposits is very rich in copper in certain zones, occurs in dolomitized carbonate host rocks that are commonly brecciated, and contains germanium-bearing copper sulfides. The ore zone at the Apex deposit, though much smaller, appears to be most like that at Kipushi, in the Zaire-Zambia copper belt. The orebody at Kipushi forms a highly irregular subvertical pipe at the faulted boundary of dolomitic shale and marine dolomite, commonly within breccia zones (Intiomale and Oosterbosch, 1974; DeVos and others, 1974). Some sulfide replacement extends along bedding planes and fracture zones. The bulk of the ore consists of the assemblages chalcopyrite-pyrite, chalcopyrite-bornite-tennantite, bornite-chalcocite, and sphalerite-pyrite-galena. Renierite, with lesser germanite and briartite ($Cu_2(Fe,Zn)GeS_4$), are locally common in copper-rich ore, commonly near zinc-rich ore. Gallite is present in small quantities as inclusions in renierite, germanite, and sphalerite.

Supergene Alteration

At the Apex Mine, supergene alteration of the ore has occurred at least down to the 1,230-m level, the maximum depth of the old workings. The water table had not yet been reached at that level. The thorough oxidation of the ore is certainly due to the high permeability of the limestone, and particularly of the fault zones, which allowed access to air, meteoritic water, and Thiobacillus bacteria that can break down sulfides (Duncan, 1967).

It is not clear if the general separation of iron-rich and copper-rich ore now observed reflects the original distribution of sulfides, or is a product of supergene alteration. The occurrence of the richest copper ore in and adjacent to carbonate rock, and the nearly complete lack of residual primary copper minerals, suggest that copper was fairly mobile during supergene alteration, and was precipitated mainly by reaction with carbonate wallrocks and breccia fragments. The similar distribution of zinc-bearing minerals to copper-bearing minerals suggests that zinc behaved in much the same way. Lead, however, was mainly precipitated in place as sulfates (plumbian jarosite and anglesite). Gallium was concentrated mainly in jarosite, where it substituted for iron, and in limonite, where it either substituted for iron or was adsorbed onto grain and fracture surfaces. Most of the iron in the ore was left in a spongy to dense mixture of limonite, goethite, and hematite.

Germanium became concentrated mainly in goethite, hematite, and limonite, though it is uncertain whether it is primarily adsorbed onto grains of these minerals or is incorporated into their lattices. Some solid solution between magnetite and the related spinel brunogeierite ($GeFe_2O_4$) has been reported (Otteman and Nuber, 1972), probably through the coupled substitution $2Fe(III) \leftrightarrow Ge(IV) + Fe(II)$. The same or similar coupled substitutions may account for the presence of germanium in goethite and hematite. Burton and others (1959), for example, reported as much as 83 ppm germanium in hematite from Cumberland, England. Experiments have shown that germanium has a high affinity for iron hydroxide: Burton and others (1959) found 95 percent of dissolved germanium to be precipitated from seawater by $Fe(OH)_3$, and Pazenkova (1963) found 93 percent of dissolved germanium to be precipitated by $Fe(OH)_3$ in waters with a pH greater than about 6; less germanium was incorporated from more acidic waters.

Implications

Future mining operations at the Apex Mine may eventually reach primary sulfide ore, which would permit better comparisons with other deposits and would allow a more thorough understanding of the supergene alteration that has occurred. Primary ore may occur below the current water table, where it would not have been exposed to severe oxidizing conditions. However, the position of the water table in the vicinity of the mine is not known. A flowing spring (Cave Spring) is located 4.9 km east of the mine at an elevation of 1,160 m (70 m below the deepest workings), and the perennial Virgin River is about 11 km to the southeast at an elevation of about 750 m (480 m below the deepest workings), which would be a minimum level for the water table.

The similarity was previously noted between the supergene ore at the Apex Mine and the gossans at many sulfide ore deposits, particularly at those containing considerable arsenic. This observation, combined with observations that germanium is commonly concentrated in carbonate-hosted copper-rich deposits, many of which are associated with organic material (Bernstein, 1985), may be useful in the exploration for additional germanium deposits. Similarly, the occurrence of gallium in jarosite-group minerals and limonite at the Apex Mine provides new directions in the exploration for this metal.

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